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Communication

Synthesis of Bis(1,2,3-triazolyl)alkanes in Superbasic and Solvent-Free Conditions

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Abstract: Nucleophilic substitution reactions between 1,2,3-triazole and dibromomethane or 1,2-dirbomoethane in a superbasic medium potassium hydroxide–dimethyl sulfoxide gave mixtures of the isomeric bis(1,2,3-triazolyl)alkanes, in which (1,2,3-triazol-1-yl)(1,2,3-triazol-2-yl)alkanes and bis(1,2,3-triazol-2-yl)alkanes were the dominating products, while bis(triazol-1-yl)alkanes were detected only in trace amounts. The same products could also be obtained under solvent-free conditions in a neat reaction mixture. The proposed methods are economically feasible, do not require using toxic solvents or catalysts, and make the (1,2,3-triazol-2-yl)-derivatives, inaccessible by alkyne-azide cycloaddition (click) reactions, readily available.

Keywords: 1,2,3-triazole; bis(1,2,3-triazol-2-yl)methane; 1,2-bis(1,2,3-triazol-2-yl)ethane; nucleophilic substitution; solvent-free synthesis; superbasic medium

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1. Introduction

1,2,3-triazole is a well-known heterocycle, the derivatives of which exhibit a variety of important properties. The discovery of the azide-alkyne cycloaddition (click reaction) rendered 1,4- and 1,5-disubstituted 1,2,3-triazoles readily available, which was followed by a large-scale study of these compounds, especially in the context of pharmaceutical and coordination chemistry [1–3]. Other applications of 1,2,3-triazoles include organic fluorophores [4] and chemosensors [5]. Compounds containing a 1,2,3-triazole ring demonstrate anticancer, anti-inflammatory, antiviral, and antibacterial activity [6]. Ligands with two or three 1,2,3-triazole rings synthesized via the click reaction became convenient building blocks for the preparation of metal-organic frameworks (MOFs) [7]. The presence of several donor nitrogen atoms and a highly polarized carbon atom ensures the coordination of the metal and association with anions both through hydrogen and halogen bonding.

Ligands containing two 4,5-unsubstituted 1,2,3-triazole rings have not been widely studied so far, and only scarce examples may be found in the literature. Thus, Bronisz et al. prepared a series of bis(1,2,3-triazol-1-yl)alkanes by alkylation of sodium triazolate, albeit in low yield. The prepared ligands were used for the synthesis of iron(II) coordination polymers, demonstrating spin-crossover [8–10]. A top-down approach was employed in [11] to prepare 1,2-bis(1,2,3-triazol-1-yl)ethane by decarboxylation of the corresponding tetracarboxylic acid.

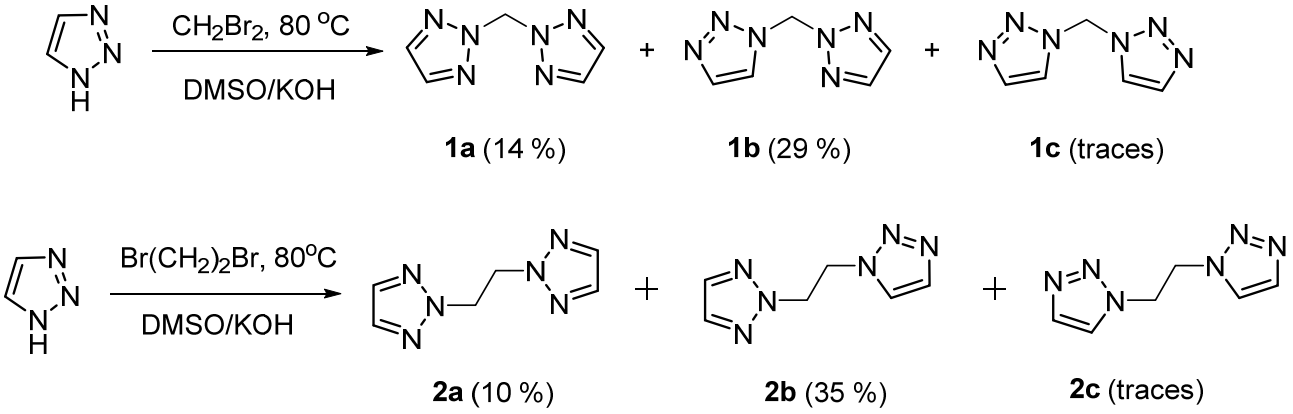
Derivatives of 1,2,3-triazole with 2-substituted heterocycles are inaccessible by a click-reaction and are prepared by alternative methods. Thus, 1-(1,2,3-triazol-1-yl)-4-(1,2,3-triazol-2-yl)butane was synthesized by nucleophilic substitution using sodium triazolate [12], and 1,6-bis(1,2,3-triazol-2-yl)hexane was obtained in the same work by the Mitsunobu reaction [12].

In addition to the above-mentioned coordination compounds with bis(1,2,3-triazol-1-yl)alkanes, coordination polymers with silver(I) [12], iron(II) [13], and zinc(II) [14,15] were reported in the literature.

Herein we propose a convenient method for the synthesis of bis(1,2,3-triazolyl)alkanes, namely bis(1,2,3-triazolyl)methanes and 1,2-bis(1,2,3-trizolyl)ethanes, in a superbasic medium and under solvent-free conditions. Superbasic mediums are defined as systems capable of ionizing weak acids to a greater extent than a 0.1 M solution of alkalis in water [16]. Usually, aprotic solvent-NaOH/KOH systems are used, and amphiphilic dimethyl sulfoxide (DMSO) is often the solvent of choice due to its low toxicity, high boiling point, and miscibility with water. The reactivity of an ionized nucleophile greatly depends on the degree of its solvation. "Hard" anions with a localized charge, such as hydroxides or alkoxides, form hydrogen bonds that are stable in aqueous and alcoholic solutions. In DMSO, they are unstable and can effectively engage in nucleophilic substitution and addition reactions [17].

2. Results and Discussion

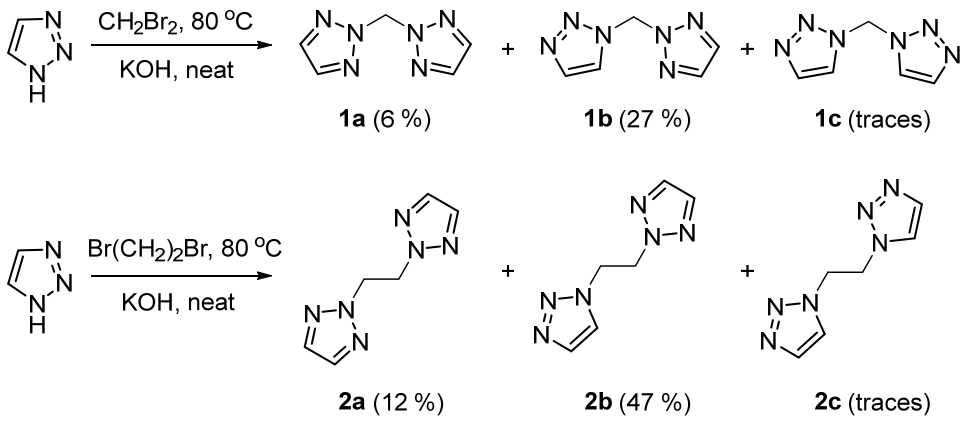
Reactions of 1,2,3-triazole with dibromomethane or 1,2-dibromoethane in a superbasic medium potassium hydroxide/dimethylsulfoxide (KOH/DMSO) at 80 °C gave the corresponding bis(1,2,3-triazolyl)alkanes **1a**–**c** and **2a**–**c** (Scheme 1). In both cases, a mixture of three isomeric products was formed, due to the existence of two tautomeric forms of 1,2,3-triazole [18,19].



Scheme 1. Synthesis of bis(1,2,3-triazolyl)alkanes in a superbasic medium.

The isomeric products were identified by gas chromatography-mass spectrometry (GC/MS) with electron-impact (EI) ionization, and individual compounds were isolated by column chromatography. The isomeric products are further referred to as 1,1-, 1,2- and 2,2-isomers depending on the substitution position in the 1,2,3-triazole ring. It is interesting to note that the 1,1-isomers **1c** and **2c** were detected only in trace quantities, in contrast to previously described reactions of 1,2,4-triazole and benzo-1,2,3-triazole, for which 1,1-substituted products were the major ones [20–23]. The different reactivity of 1,2,3-triazole is probably explained by the greater thermodynamic stability of the 2H-1,2,3-triazolyl anion compared to the 1H form [24,25].

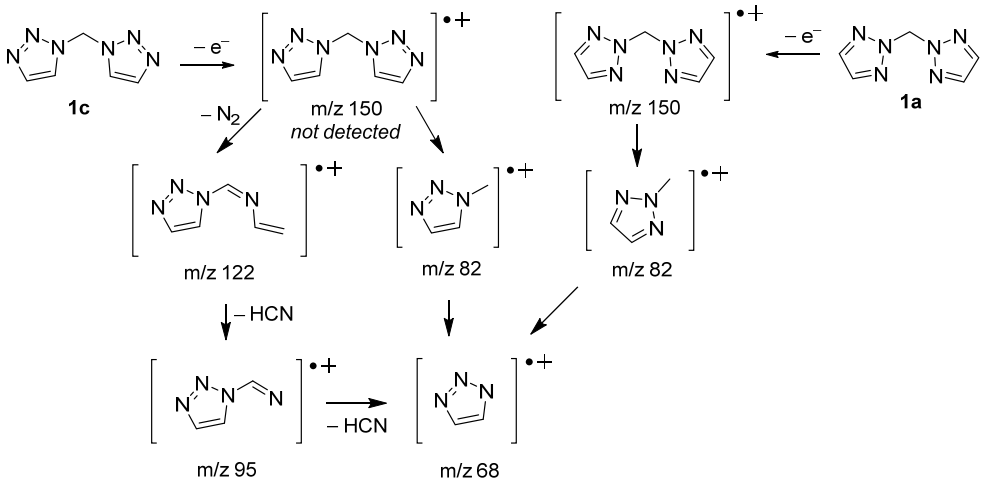
An alternative way to obtain compounds **1** and **2** is carrying out the reaction in the absence of solvent since both 1,2,3-triazole and dihalogenoalkanes are liquids at room temperature (Scheme 2). The composition of the products under solvent-free conditions and in DMSO is qualitatively similar, but the relative amounts are slightly different, which is probably due to the different relative stabilities of the intermediate monoalkylated products in DMSO and the neat reaction mixture.



Scheme 2. Synthesis of bis(1,2,3-triazolyl)alkanes under solvent-free conditions.

The structure of individual bis(1,2,3-triazolyl)alkanes isolated by column chromatography was confirmed by NMR ^{1}H and ^{13}C spectrometry, as well as by mass spectrometry.

Mass spectrometry with electron impact ionization was found to be useful for the identification of the isomeric bis(1,2,3-triazolyl)alkanes. The mass spectra of bis(1,2,3-triazolyl)methanes and 1,2-bis(1,2,3-triazolyl)ethanes are shown in Figures S1–S3. The fragmentation pathways of the molecular ions, [M^{+}], of compounds **1** and **2** are similar and will be discussed here for bis(1,2,3-triazolyl)methane isomers (**1a**–**c**). A stable molecular ion (*m*/*z* 150) was only detected in the EI mass spectrum of 2,2-isomer **1a** (Scheme 3). Apparently, this is due to the ease with which the dinitrogen (N_2) molecule was eliminated from the [M^{+}] ion of the 1,1-isomer **1c** with the formation of a fairly stable radical cation (*m*/*z* 122) (Scheme 3), the heaviest peak in the mass spectrum of this compound (Figure S1). Subsequently, this ion releases the HCN molecule and forms a triazolium radical cation (*m*/*z* 68). The molecular ions of 2-substituted isomers **1a** and **1b** undergo an alternative fragmentation pathway through the cleavage of the C(sp^3)-N(sp^2) bond (Scheme 3). The triazolium radical cation shows the highest intensity in the mass spectrum of 1,1-isomer, while the signal of the methylene triazolium radical cation has the highest intensity in the mass spectra of the other two isomers. Therefore, GC/MS allows to reliability distinguish the isomeric bis(1,2,3-triazolyl)alkanes.



Scheme 3. Possible fragmentation scheme of the molecular ion of isomeric bis(1,2,3-triazolyl)methanes.

The NMR ^{1}H and ^{13}C spectra of compounds **1a-b** and **2a-b** are in accordance with their structures (Figures S4–S11). The ^{1}H-NMR spectra of bis(1,2,3-triazol-2-yl)alkanes **1a** and **2a** contain one signal due to the aromatic protons of the 1,2,3-triazole rings at 7.6–7.6 ppm, this

signal is shifted upfield in the ethane derivative **2a** due to weaker electron-withdrawing influence of the second heterocycle through two methylene groups. The doublets due to two inequivalent protons of 1,2,3-triazol-1-yl rings in 1,2-isomer **1b** were registered at 7.71 and 7.84 ppm and were again shifted upfield to 7.24 and 7.62 ppm in the spectrum of compound **2b**.

The FT-IR spectra of bis(1,2,3-triazolyl)alkanes (Figures S12–S15) contain the characteristic bands of the C–H stretching vibrations near 2990 cm^{-1} for the methylene groups and in the range of 3140–3040 cm^{-1} for 1,2,3-triazole rings. The absorption bands near 1430, 1385, 1410, and 1340 cm^{-1} are the result of skeletal stretching vibrations of the heterocycle, while the bands near 1240, 1180, and 1065 cm^{-1} are due to "breathing" vibrations of the ring and C–H in-plane bending vibrations in 1,2,3-triazole rings. Strong bands in the lower frequency region at 830, 775, and 750 cm^{-1} correspond to C–H out-of-plane bending vibrations of the ring [26].

3. Materials and Methods

3.1. Instrumental Methods

Gas chromatography-mass spectrometry analysis was performed using an Agilent 7890A gas chromatograph (Agilent, Santa Clara, CA, USA) equipped with an Agilent MSD 5975C mass-selective detector with a quadrupole mass-analyzer (electron impact ionization energy of 70 eV), software version ChemStation MSD E.02.00.493. The injector temperature was maintained at 300 °C, and the injection volume was 1 μL (split 40:1). The instrument was equipped with an HP-5 ms capillary column of 30 m length, 0.25 mm i.d., and 0.25 μm film thickness. The carrier gas was helium at a constant flow rate of 1 mL/min. The GC oven program started at 79 °C (1.0 min hold) and ramped up to 300 °C (heating rate 13 °C/min) for 10 min, and the total chromatogram time was 28 min. Transfer line temperature was 300 °C; MS Source—230 °C, and MS Quadrouple—150 °C. The electron energy was 70 eV. From 0 to 4 min, the MS was switched off (solvent delay). Data analysis and instrument control were carried out with MSD 5975C software.

NMR spectra were recorded on Bruker DRX400 and Bruker Advance 500 instruments (Billerica, MA, USA), and solvent residual peaks were used as internal standards. Elemental analyses were carried out on a Vario Micro-Cube analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany). IR-spectra of solid samples were recorded on an Agilent Cary 630 FT IR (Santa Clara, CA, USA) spectrophotometer equipped with a diamond ATR accessory.

3.2. Synthetic Procedures

The starting materials and solvents of at least reagent grade were obtained from commercial sources and were used without further purification, except for DMSO, which was distilled in vacuo (5–10 mbar) over KOH.

3.2.1. Preparation of Bis(1,2,3-triazolyl)methane Isomers

Method A (in DMSO). Finely powdered KOH (0.84 g, 15 mmol) was suspended in 3 mL of DMSO, 1,2,3-triazole (0.58 mL, 10 mmol) was added, and the mixture was heated under vigorous stirring at 80 °C for 30 min to achieve equilibration. After that, the reaction mixture was cooled in a water bath to room temperature, and a solution of dibromomethane (0.38 mL, 5 mmol) in 2 mL of DMSO was added dropwise for 30 min, while the reaction flask was kept in a cool water bath. After the addition was complete, heating and stirring at 80 °C were resumed for 24 h, after which the reaction mixture was poured into 50 mL of water and extracted with chloroform (3 × 15 mL). The extract was dried over anhydrous $CaCl_2$ and the solvent was removed on a rotary evaporator. The mixture of isomers was separated by column chromatography on silica using ethyl acetate:chloroform, 2:5, as the eluent.

Method B (solvent-free conditions). Finely powdered KOH (0.84 g, 15 mmol), 1,2,3-triazole (0.58 mL, 10 mmol), and dibromomethane (0.38 mL, 5 mmol) were loaded into a

screw-cap glass vial, sealed, and heated in an oven at 80 °C for 24 h. The products were then isolated as described in Method A.

Bis(1,2,3-triazol-2-yl)methane (1a). Yield 14% (method A), 6% (method A), colorless crystals, m.p. 103–105 °C. $C_5H_6N_6$: calcd. C 40.00%; H 4.03%; N 55.97%; found C 40.4%; H 3.8%; N 55.9%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.86 (s, 2H, CH_2), 7.69 (s, 4H, $H^{3,4}$(2-Tr)) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 68.6 (CH_2), 136.3 ($C^{3,4}$(2-Tr)) ppm. FT-IR (cm^{-1}): 3139 w, 3129 w, 3046 m, 2992 w, 1429 m, 1411 s, 1384 m, 1339 s, 1242 m, 1183 s, 1065 m, 964 s, 952 s, 827 s, 775 s, 747 s, 666 s, 653 s.

(1,2,3-Triazol-1-yl)(1,2,3-triazol-2-yl)methane (1b). Yield 29% (method A), 27% (method B), colorless crystals, m.p. 85–86 °C. $C_5H_6N_6$: calcd. C 40.00%; H 4.03%; N 55.97%; found C 40.3%; H 3.8%; N 55.7%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.87 (s, 2H, CH_2), 7.69 (s, 2H, $H^{3,4}$(2-Tr)), 7.71 (d, 1H, H^5(1-Tr), J=1 Hz), 7.84 (d, 1H, H^4(1-Tr), J=1 Hz) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 64.6 (CH_2), 123.9 (C^5(1-Tr)), 134.8 (C^4(1-Tr)), 136.6 ($C^{3,4}$(2-Tr)) ppm. FT-IR (cm^{-1}): 3139 w, 3119 m, 3039 w, 2988 w, 1485 w, 1458 m, 1413 m, 1350 s, 1306 m, 1268 m, 1213 m, 1198 s, 1109 m, 1074 s, 1027 m, 960 s, 939 m, 832 s, 805 s, 777 s, 734 s, 697 m, 654 s.

Bis(1,2,3-triazol-1-yl)methane (1c). This isomer was formed in trace amounts and only detected by GC/MS. *m*/*z*: 150 $(M)^+$, 94, 82, 70, 69, 68, 55.

3.2.2. Preparation of 1,2-Bis(1,2,3-triazolyl)ethane Isomers

Compounds **2a-2c** were prepared as described above (Methods A and B) for products **1a-1c**, only 1,2-dibromoethane was used instead of dibromomethane.

1,2-Bis(1,2,3-triazol-2-yl)ethane (2a). Yield 10% (method A), 12% (method B), colorless crystals, m.p. 106–108 °C. $C_6H_8N_6$: calcd. C 43.90%; H 4.91%; N 51.19%; found C 44.0%; H 4.8%; N 51.2%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.00 (s, 4H, CH_2), 7.57 (s, 4H, $H^{3,4}$(2-Tr)) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 53.8 (CH_2), 134.8 ($C^{3,4}$(Tr)) ppm. FT-IR (cm^{-1}): 3130 w, 3117 m, 1456 m, 1421 m, 1363 s, 1213 m, 1104 m, 1087 m, 974 s, 961 s, 831 s, 711 s, 669 s.

1-(1,2,3-Triazol-1-yl)-2-(1,2,3-triazol-2-yl)ethane (2b). Yield 35% (method A), 47% (method B), colorless crystals, m.p. 90–91 °C. $C_5H_6N_6$: calcd. C 43.90%; H 4.91%; N 51.19%; found C 44.1%; H 4.7%; N 51.0%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.92–5.02 (m, 4H, CH_2), 7.24 (d, 1H, H^5(1-Tr), J = 0.5 Hz), 7.60 (s, 2H, $H^{3,4}$(2-Tr)), 7.62 (d, 1H, H^4(1-Tr), J = 0.5 Hz) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 49.2 (1-Tr-CH_2), 54.2 (2-Tr-CH_2), 124.3 (C^5(1-Tr)), 133.7 (C^4(1-Tr)), 135.1 ($C^{4,5}$(2-Tr)) ppm. FT-IR (cm^{-1}): 3129 w, 3117 w, 3101 m, 1492 m, 1469 m, 1457 m, 1421 m, 1361 s, 1288 m, 1243 w, 1214 m, 1202 m, 1126 s, 1088 s, 1025 s, 977 m, 960 s, 836 s, 819 s, 804 s, 699 s, 668 s.

1,2,Bis(1,2,3-triazol-1-yl) ethane (2c). This isomer was formed in trace amounts and only detected by GC/MS. *m*/*z*: 136, 107, 96, 82, 67, 54.

4. Conclusions

In summary, synthetic approaches to individual bis(1,2,3-triazol-2-yl)alkanes by nucleophilic substitution in a superbasic medium and in solvent-free conditions. It was found that compounds containing (1,2,3-triazol-2-yl) cycles dominate in the product mixtures, and the individual isomers were isolated by column chromatography. The structure of the products was confirmed by FT-IR spectroscopy, mass spectrometry, and NMR spectrometry. The proposed methods do not require using toxic or expensive solvents and catalysts and thus make the bis(1,2,3-triazol-2-yl)alkanes readily available compounds.

Supplementary Materials: The following supporting information can be downloaded online, Figure S1. Electron impact (70 eV) mass spectra of isomeric bis(1,2,3-triazolyl)methanes 1a-1c; Figure S2. Electron impact (70 eV) mass spectrum of 1,2-bis(1,2,3-triazol-2-yl)ethane **2a**; Figure S3. Electron impact (70 eV) mass spectrum of 1-(1,2,3-triazol-1-yl)-2-(1,2,3-triazol-2-yl)ethane **2b**; Figure S4. ^{1}H NMR spectrum (500 MHz, in $CDCl_3$) of bis(1,2,3-triazol-2-yl)methane 1a; Figure S5. ^{13}C NMR spectrum (125 MHz, in $CDCl_3$) of bis(1,2,3-triazol-2-yl)methane 1a; Figure S6. ^{1}H NMR spectrum (500 MHz, in $CDCl_3$) of (1,2,3-triazol-1-yl)(1,2,3-triazol-2-yl)methane 1b; Figure S7. ^{13}C NMR spectrum (125 MHz, in $CDCl_3$) of (1,2,3-triazol-1-yl)(1,2,3-triazol-2-yl)methane 1b; Figure S8.

^{1}H NMR spectrum (500 MHz, in $CDCl_3$) of 1,2-bis(1,2,3-triazol-2-yl)ethane **2a**; Figure S9. ^{13}C NMR spectrum (150 MHz, in $CDCl_3$) of 1,2-bis(1,2,3-triazol-2-yl)ethane **2a**; Figure S10. ^{1}H NMR spectrum (500 MHz, in $CDCl_3$) of 1-(1,2,3-triazol-1-yl)-2-(1,2,3-triazol-2-yl)ethane **2b**; Figure S11. ^{13}C NMR spectrum (150 MHz, in $CDCl_3$) of 1-(1,2,3-triazol-1-yl)-2-(1,2,3-triazol-2-yl)ethane **2b**; Figure S12. FT-IR spectrum of bis(1,2,3-triazol-2-yl)methane 1a; Figure S13. FT-IR spectrum of (1,2,3-triazol-1-yl)(1,2,3-triazol-2-yl)methane 1b; Figure S14. FT-IR spectrum of 1,2-(1,2,3-triazol-2-yl)ethane **2a**; Figure S15. FT-IR spectrum of 1-(1,2,3-triazol-1-yl)-2-(1,2,3-triazol-2-yl)methane **2b**.

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